UNCATALYZED REACTION OF SELECTED UNSATURATED COMPOUNDS WITH D_2

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INTRODUCTION

In our previous study of the reaction of 1,2-diphenylethane (bibenzyl), **DPE**,[1] and other compounds[2] with D_2 at temperatures to 450 °C and pressures of 2000 psi in isolation from metal surfaces, we were able to provide strong evidence for a mechanistic scheme wherein radicals formed by the homolysis of weak bonds, react with D_2 to give D atoms. These participate in short radical-chain processes responsible for hydrocracking and exchange of H for D at unsubstituted aromatic positions. In contrast to the simple thermolysis of **DPE** wherein stilbene (PhCH=CHPh), **STB**, is formed as a major product, the reaction of **DPE** with D_2 produces relatively small amounts of this compound. Moreover, the mole % of **STB** among the products decreases as conversion increases, indicating that initially produced **STB** is consumed. It, therefore, seemed important to examine the reaction of **STB** with D_2. This study has subsequently been extended to other unsaturated compounds and the results are reported below.

EXPERIMENTAL

Reaction Procedure. Reactions were carried out as described earlier,[1] placing the reactants along with glass beads for agitation in a glass bulb (ca. 12 mL) with a long capillary neck. The vessel was then suspended in glass wool in the interior of a stainless steel reaction tube having a long neck to house the capillary section of the vessel. The entire apparatus was evacuated, pressured with D_2 gas, closed off and shaken at the desired temperature in a fluidized sand bath. Temperatures reported were corrected from bath calibrations using a thermocouple-containing reactor and were measured under H_2. Times reported are actual time-in-bath measurements and should be shortened by approximately 5 min to allow for a measured 8 min heat-up period. When the heating period was complete, carbon disulfide was added and products removed for analysis using a long syringe needle. In the absence of gas generation within the tube, our observation has been that at least for high concentration runs, an insignificant amount of material is lost from the interior of the bulb. Control experiments in which a hydrogenation catalyst was deliberately added showed complete saturation of aromatic compounds under the reaction conditions. Product mixtures were analyzed by gas chromatography (GC) and by gas chromatography/mass spectrometry (GC/MS). Products present in substantial quantities were separated by preparative gas chromatography and analyzed by ^1H and ^2H NMR at 400 MHz in carbon disulfide. cis-Stilbene did not separate from **DPE** by GC, but was determined from mass spectral analysis using calibrating mixtures of these compounds.

Reactants. Reactants were generally the best quality of commercially-available material. 1-methylstyrene was distilled to remove polymerization inhibitor. Several grades of trans-stilbene were tested and, as all contained small amounts of **DPE**, this compound was synthesized by a modified Wittig synthesis to produce **DPE**-free material.[3] The synthetic material was a mixture of cis- and trans-stilbene, but had no effect on reaction outcome because equilibrium between these two isomers was attained early in the reaction period.

RESULTS AND DISCUSSION

Table I presents data for reaction of several unsaturated compounds with D_2 at 2000 psi and 410 °C. It will be noted that for the four compounds studied to date, **STB**; α-methylstyrene ($Ph(CH_3)C{=}CH_2$), **MS**; anthracene, **AN**; and phenanthrene, **PN**; all except **PN** show substantial reaction with D_2 at 410 °C. The reactive compounds produce dihydro products which contain D atoms as well as incorporating deuterium themselves.

General Mechanistic Considerations. It was demonstrated in our earlier studies that D atoms add reversibly to phenyl rings in **DPE** and its hydrothermolysis products by eqs 1 and 2.

$$D\bullet \quad + \quad H\text{-}Ar \quad \text{-->} \quad H\bullet \quad + \quad D\text{-}Ar \qquad (1)$$

$$H\bullet \quad + \quad D_2 \quad \text{-->} \quad H\text{-}D \quad + \quad D\bullet \qquad (2)$$

As double bonds, lacking the resonance stability of benzene rings are certain to at least equally reactive toward D atoms, it seems clear that the general process of eq 3 will be important if D atoms are present.

$$D\bullet \quad + \quad C{=}C \quad \text{-->} \quad D\text{-}C\text{-}C\bullet \qquad (3)$$

The radicals generated in eq 3 would then be expected to either undergo the reaction of eq 4, completing a kinetic-chain sequence, or undergo termination either by coupling or disproportionation. As coupling would be a reversible process under the conditions of this study, it is necessary only to consider disproportionation, eq 5.

$$D\text{-}C\text{-}C\bullet \quad + \quad D_2 \quad \text{-->} \quad D\text{-}C\text{-}C\text{-}D \quad + \quad D\bullet \qquad (4)$$

$$2\ D\text{-}C\text{-}C\bullet \quad \text{-->} \quad D\text{-}C\text{-}C\text{-}(D \text{ or } H) \quad + \quad C{=}C(D \text{ or } H) \qquad (5)$$

Several alternative mechanisms are possible. For the extreme case in which eqs 3 and 4 are fast and irreversible, dihydrocompounds containing exactly two D atoms would be obtained and there would be no D in recovered C=C. Clearly, this situation does not transpire for any of the reactions in Table I. In principle it should be possible to determine the extent to which products were formed via eq 5 from the amount of D introduced into recovered C=C. However, the analysis is confounded by the fact that aromatic exchange is expected via eqs 1 and 2. Of course, it is always possible that radical processes are not involved and that the reaction of C=C with D_2 would occur by a one-step cycloaddition process. In such a process one might expect to see simple second-order kinetics and no introduction of D atoms at sites other than those directly involved in the hydrogen transfer.

Stilbene, STB. The data presented in Table I show that **STB** is reduced to **DPE** and a total of approximately 2 atoms of D are introduced in the combined products. While it is difficult to distinguish aromatic and vinylic D in recovered stilbene, ^2H NMR shows 0.37 atoms of aromatic D in **DPE** produced in runs comparable to those in Table I. As aromatic sites in **STB** and **DPE** should have comparable reactivity with D atoms, most of the D in recovered stilbene seems likely to be at aromatic sites. Consistent with this, an ^2H NMR upper limit for vinyl D in stilbene at <0.05 atoms can be established. This suggests that products formed via eq 5 make a relatively minor contribution when low concentrations of **STB** are present.

A complication for **STB** is that as **DPE** is produced it undergoes thermolysis by processes detailed earlier.[1] In fact, under conditions only slightly more vigorous than those of Table I, stilbene can be completely converted to a mixture of **DPE** and its hydrothermolysis products with very high D content (average of 8.6 atoms of D in **DPE**). It seems likely that once **DPE** is produced in the reaction mixture, radicals produced in its thermolysis constitute the major initiating species via reaction with D_2 followed by the sequence of eqs 3 and 4. The question of how the process is initiated in the absence of all radical producing species is difficult to answer. The third entry of Table I shows that **DPE** is produced even when synthetic **STB** (free of **DPE** to detection limits) is employed.

Despite the complexities discussed, the strong concentration dependence of the reaction suggests that chains of moderate length are operative at low concentration. At low concentrations, we suggest that the predominant pathway for the reaction of **STB** with D_2 involves the sequence of eqs 3 and 4 plus some reaction with H atoms when these are generated by eq 1. When the initial concentration is increased, the efficiency of conversion to **DPE** is reduced by higher radical concentrations which increase competition by eq 5.

α-Methylstyrene, MS. On comparable treatment with D_2, **MS** produces cumene. However the D content is less than observed for **DPE** from **STB** and decreases with increasing concentration of **MS**. For the higher concentration runs of Table I, the D atom content of cumene plus **MS** is close to 1 atom per equivalent of cumene formed. This is different from **STB** and **AN** for which two or more atoms of D are incorporated. This lower D incorporation suggests chain transfer involving **MS** as shown in eq 6 forming monodeuterated cumene and the 2-phenylallyl radical. It will be noted that for **STB** and **AN**, the substrate is unlikely to act as an H-atom donor.

$$Ph(CH_3)(CH_2D)C\bullet + Ph(CH_3)C{=}CH_2 \rightarrow Ph(CH_3)(CH_2D)C\text{-}H + Ph(H_2C{=})C\text{-}CH_2\bullet \qquad (6)$$

It seems likely that the 2-phenylallyl radical thus formed reacts with **MS** to give higher molecular weight products as these are found in nearly equal amount to cumene and increase with increasing concentration of **MS** as might be expected. It will be noted that this substrate is the only one studied for which conversion increases with amount used.

Earlier study of the thermolysis of bicumyl ($Ph(CH_3)_2C\text{-}C(CH_3)_2Ph$) under D_2 has shown that cumyl radicals ($Ph(CH_3)_2C\bullet$) are relatively reluctant participants in the reaction of eq 4.[4] This being the case, it might be expected that eq 5 is the major route to product formation. However, such a scheme should lead to more D in recovered **MS** than observed. Perhaps because of the higher temperature and lower radical concentrations here, as contrasted with the bicumyl experiments, eq 4 becomes more competitive.

In contrast to the case of **SB**, the hydrogenation product from **MS** (cumene) would not seem to be capable of serving as an initiator, thus requiring some different type of initiation step. We suggest the reaction of eq 7 in which two molecules of **MS** undergo a "molecular disproportionation" reaction to give the 2-phenylallyl radical ($Ph(H_2C{=})C\text{-}CH_2\bullet$) and a cumyl radical.

$$2\ Ph(CH_3)C{=}CH_2 \rightarrow Ph(H_2C{=})C\text{-}CH_2\bullet + Ph(CH_3)_2C\bullet \qquad (7)$$

The cumene formed via eq 6 would be monodeuterated but, to the extent that eq 6 was a viable path for the cumyl radical formed in eq 7, some of the cumene would be produced without deuterium. Significantly, the predominant cumene isotopomer is d_1 in the 50 mg run but d_0 in the 300 mg run.

Anthracene, AN. Under the same conditions, **AN** reacts with D_2 to give dihydroanthracene, **ANH$_2$** (taken to include ANHD, AND_2, etc.). This reaction has been reported earlier with H_2 at 430 °C in methylnaphthalene solvent.[5] The total amount of D incorporated in **AN** plus **ANH$_2$** was to 2.1 to 2.6 atoms of D per equivalent of **ANH$_2$** produced. This reaction shows no significant concentration dependence and, therefore seems unlikely to be a kinetic chain process. The mechanism probable for the preceding systems in which D atoms add to **AN** to form adduct radicals, **AND•**, and these disproportionate as shown in eq 8 is one possibility.

$$2\ \mathbf{AND}\bullet \rightarrow \mathbf{AN} + \mathbf{ANHD}\ (\text{or } \mathbf{AN\text{-}d_1} + \mathbf{ANH_2}) \qquad (8)$$

If this mechanism is correct, it is necessary to account for the initial production of D atoms. Coupling of two **AN** molecules as reported by Stein[6] is a possibility. The reaction of eq 8 is known to be reversible[7] so that once **ANH$_2$** and its isotopomers are formed, exchange of H and D atoms would be rapid and, moreover, this will occur via a radical mechanism. The question which remains is whether the adduct radicals (**ANH•** and **AND•**) are sufficiently reactive to remove D atoms from D_2. While further experiments will be required to answer this question definitively, it is significant that ^{2}H NMR studies show that there is very little aromatic D in **ANH$_2$**. Also the D atoms in recovered **AN** are located to >80% (detection limit) in the 9,10-positions. A mechanism wherein half of the deuterium incorporated arrives as D atoms can be reconciled with these observations only if D atoms are highly selective for the 9,10-positions.

One possibility which cannot be discounted by any of the evidence presently at hand. is that the addition of D_2 to **AN** is a 2 + 4 cycloaddition. It is the only system in this study for which cycloaddition to give a stable product is symmetry allowed.

Phenanthrene, PN. **PN** does not react under these conditions. The fact that **AN** does react could be taken as evidence for 2 + 4 cycloaddition which is not symmetry allowed for **PN**. On the other hand, the 9,10-positions in **AN** are notoriously reactive[7d] and initiation processes with **AN** might be more effective than comparable reactions with **PN**. The striking difference in reactivity of these two compounds will require further study for complete analysis.

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SUMMARY

The reaction of D_2 with several unsaturated substrates has been documented. The reaction involved no intentionally added hydrogenation catalyst and, with the possible exception of **AN**, is believed to involve D atom addition to the unsaturated compound with the resultant adduct radical either reacting with D_2 or undergoing disproportionation. In the case of anthracene, the results are consistent with a direct 2 + 4 cycloaddition.

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Table I. Reaction of Unsaturated Compounds with D_2 (2000 psi) at 410 °C for 20 min.[a]

Compound	Amount[b] (mg)	% H-C-C-H[d]	D atoms in H-C-C-H[c]	D atoms in C=C[c]
STB	25[e]	22[g]	1.67	0.23
STB	50[f]	13[g]	1.47	0.10
STB	25[f]	22[g]	1.73	0.22
STB	50	5.4[k]	1.5[j]	<0.03
STB	100	1.8	1.5[j]	<0.01
MS	50	14[h]	1.34	0.13
MS	150	18[h]	0.80	0.09
MS	300	27[h]	0.65	0.16
AN	50	33[i]	1.55	0.37
AN	100	35[i]	1.20	0.48
AN	300	26[i]	1.10	0.57
PHN	50	<0.2	---	<0.05
PHN	100	<0.2	---	<0.05
PHN	300	<0.2	---	<0.05

[a] The 20 min time period refers to the time after temperature equilbrium is reached inside of the cell. There is an 8 min heat-up period. [b] This is the weight of material inside of an approximately 12 mL reaction vessel. [c] Average number of D atoms per molecule as determined by GC/MS analysis. [d] Balance of material is recovered C=C, except as otherwise noted. [e] Commercial material contains 0.7% of **DPE**. [f] Synthetic material contains < 0.01% **DPE**. [g] Product mixture also contains 5 - 10% of products of **DPE** reaction (benzene, toluene, ethylbenzene, styrene, 1,1-diphenylethane, diphenylmethane, etc. [h] Similar amounts (12, 17 and 21%) of other products, most of which appeared to be dimers and dehydrodimers of expected intermediate radicals. [i] Tetrahydroanthracenes were formed in amounts of up to 3% increasing with increasing concentration. [j] Corrected for **DPE** in starting **STB**. [k] This run should be the same as the previous 50 mg run, but gave lower conversion. It is believed that this is due to temperature variations. The first three **STB** runs were carried out on a different day from the last two.